

DESCRIPTION

POLYESTER FIBER STRUCTURE5 Technical Field

The present invention relates to a polyester fiber structure. More specifically, it relates to a polyester fiber structure produced using a polyester resin with satisfactory color tone and excellent moldability.

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10 Background Art

Polyester resins, and particularly polyethylene terephthalate, polyethylene naphthalate, polytrimethylene terephthalate and polytetramethylene terephthalate resins, exhibit excellent mechanical, physical and chemical performance and are therefore widely used for fibers, films and other molded products. Especially when used in fiber structures, they are known to exhibit excellent mechanical strength and dimensional stability.

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Such polymers for fiber structures, for example polyethylene terephthalate, are usually produced by first preparing an ethylene glycol ester of terephthalic acid and/or a lower polymer thereof and then heating it under reduced pressure in the presence of a polymerization catalyst for reaction to the desired degree of polymerization. Other polyesters are produced by similar processes.

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It is known that the type of polycondensation catalyst used has a major effect on the quality of the resulting polyester, and antimony compounds are most widely used as polycondensation catalysts for polyethylene terephthalate.

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A problem is associated with the use of antimony compounds, however, because prolonged continuous melt spinning of polyesters results in accumulated adhesion of foreign matter around the spinneret hole (hereinafter referred to simply as "spinneret adhesion" and

redirection of the molten polymer flow (bending), which ultimately lead to fluff and yarn breakage or mottling of the physical properties of the fiber during the spinning and stretching steps. In addition, using polyester
5 fibers comprising such polyesters for production of polyester fiber structures has resulted in problems such as poor process stability and low quality of the obtained polyester fiber structures.

As a means of solving these problems, there have
10 been disclosed the use of the reaction products of titanium compounds and trimellitic acid as polyester production catalysts (for example, see Patent Document 1) and the use of the reaction products of titanium compounds and phosphorous acid esters as polyester
15 production catalysts (for example, see Patent Document 2). While these methods do enhance the molten heat stability of polyesters to some degree, the enhancing effect is inadequate and the obtained polyester resins are in need of color tone improvement.
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There have also been proposed titanium compound/phosphorus compound complexes as polyester production catalysts (for example, see Patent Document 3). However, although this method enhances the molten heat stability to some degree, the effect has been
25 inadequate and the obtained polyesters are in need of color tone improvement.

[Patent Document 1]

Japanese Examined Patent Publication SHO No. 59-46258

30 [Patent Document 2]

Japanese Unexamined Patent Publication SHO No. 58-38722

[Patent Document 3]

35 Japanese Unexamined Patent Publication HEI No. 7-138354

Disclosure of the Invention

It is an object of the invention to solve the aforementioned problems of the prior art by providing a polyester fiber structure having satisfactory color tone (a high L* value and a low b* value), produced from high quality polyester fiber.

The polyester fiber structure of the invention is a polyester fiber structure comprising polyester fiber containing a polyester polymer as the major component, characterized in that

the fiber structure is at least one type of fiber structure selected from the group consisting of nonwoven fabrics comprising the polyester fiber, waddings comprising the polyester fiber and fiber structures having thicknesses of 5-100 mm, comprising main fiber made of polyester stable fiber and thermal bonding conjugated staple fiber wherein the polyester polymer is present in either or both the main fiber and the thermal bonding composite stable fiber,

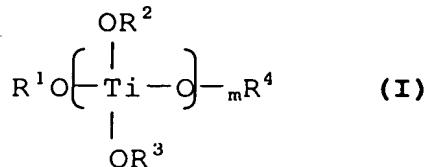
the polyester polymer is obtained by polycondensation of an aromatic dicarboxylate ester in the presence of a catalyst,

the catalyst comprises at least one ingredient selected from among mixture (1) and reaction product (2) below,

mixture (1) is a mixture of the following components (A) and (B):

(A) a titanium compound component composed of at least one compound selected from the group consisting of:

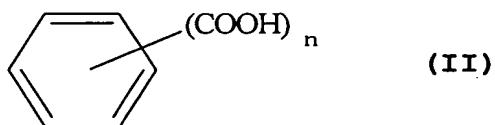
(a) titanium alkoxides represented by the following general formula (I):



[wherein R¹, R², R³ and R⁴ each independently represent one species selected from among C₁₋₂₀ alkyl groups and phenyl groups, m represents an integer of 1-4, and when m is an integer of 2, 3 or 4, the two, three or four R² and R³ groups may be the same or different], and

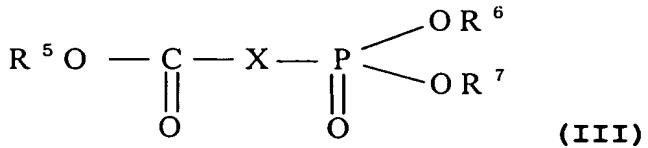
(b) reaction products of titanium alkoxides of general formula (I) above with aromatic polyvalent carboxylic acids represented by the following general formula (II):

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[wherein n represents an integer of 2-4] or their anhydrides, and

15 (B) a phosphorus compound component composed of at least one compound represented by the following general formula (III):



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[wherein R⁵, R⁶ and R⁷ each independently represent C₁₋₄ alkyl, and X represents at least one species selected from among -CH₂- and -CH₂(Y) (where Y represents phenyl)],

25 mixture (1) is used with a mixing ratio such that the ratio (%) M_{Ti} of the millimoles of elemental titanium in the titanium compound component (A) with respect to the number of moles of the aromatic dicarboxylate ester and the ratio (%) M_P of the millimoles of elemental phosphorus in the phosphorus compound component (B) with respect to the number of moles of the aromatic dicarboxylate ester satisfy the following relational expressions (i) and (ii):

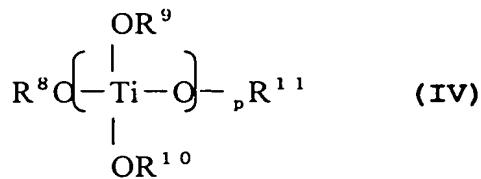
$$1 \leq M_p/M_{Ti} \leq 15 \quad (i)$$

$$10 \leq M_p + M_{Ti} \leq 100 \quad (\text{ii}),$$

and reaction product (2) is the reaction product of the following components (C) and (D):

5 (C) a titanium compound component composed of at least one compound selected from the group consisting of:

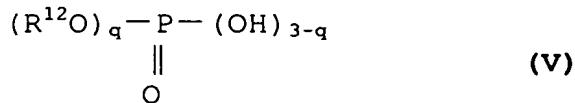
(c) titanium alkoxides represented by the following general formula (IV):



10 [wherein R⁸, R⁹, R¹⁰ and R¹¹ each independently represent C₁₋₂₀ alkyl, p represents an integer of 1-3, and when p is 2 or 3, the two or three R⁹ and R¹⁰ groups may be the same or different], and

15 (d) reaction products of titanium alkoxides of general formula (IV) above with aromatic polyvalent carboxylic acids represented by general formula (II) above or their anhydrides, and

20 (D) a phosphorus compound component composed of at least one phosphorus compound represented by the following general formula (V):



25 [wherein R¹² represents C₁₋₂₀ alkyl or C₆₋₂₀ aryl, and q represents an integer of 1 or 2].

Component (A) of the catalyst mixture (1) and component (C) of the reaction product (2) for the catalyst in the polyester fiber structure of the invention preferably contain the respective titanium alkoxide (a) and titanium alkoxide (c) each in a reaction molar ratio in the range of 2:1 to 2:5 with respect to the aromatic polyvalent carboxylic acid or its anhydride.

5 In the reaction product (2) for the catalyst of the polyester fiber structure of the invention, the reaction ratio of component (D) with respect to component (C) is preferably in the range of 1:1 to 3:1, in terms of the ratio of the moles of phosphorus atoms in component (D) to the moles of titanium atoms in component (C) (P/Ti).

10 The phosphorus compound of general formula (V) for reaction product (2) in the polyester fiber structure of the invention is preferably selected from among monoalkyl phosphates.

15 The aromatic dicarboxylate ester in the polyester fiber structure of the invention is preferably produced by transesterification of an aromatic dicarboxylic acid dialkyl ester and an alkylene glycol ester.

20 The aromatic dicarboxylic acid in the polyester fiber structure of the invention is preferably selected from among terephthalic acid, 1,2-naphthalenedicarboxylic acid, phthalic acid, isophthalic acid, diphenyldicarboxylic acid and diphenoxymethanedicarboxylic acid, and the alkylene glycol is preferably selected from among ethylene glycol, butylene glycol, trimethylene glycol, propylene glycol, neopentyl glycol, hexanemethylene glycol and dodecanemethylene glycol.

25 The polyester polymer of the polyester fiber structure of the invention preferably has an L* value of 77-85 and a b* value of 2-5 based on the L*a*b* color system (JIS Z8729).

30 The thermal bonding conjugated staple fiber of the polyester fiber structure of the invention may have a side-by-side structure, or the thermal bonding conjugated staple fiber may have a concentric or eccentric core-sheath structure, where the concentric or eccentric core may be formed of a fiber-forming thermoplastic polymer and the concentric or eccentric sheath may be formed of a heat sealing polymer.

35 In the polyester fiber structure of the invention, the fiber-forming thermoplastic polymer of the thermal

5 bonding conjugated staple fiber is preferably a polyester polymer. The heat sealing polymer of the thermal bonding conjugated staple fiber is preferably selected from among polyurethane elastomers, polyester elastomers, inelastic polyester homopolymers and copolymers, polyolefin homopolymers and copolymers, and polyvinyl alcohol polymers.

10 A fiber structure with a thickness of 5-100 mm in a polyester fiber structure according to the invention is preferably thermally anchored at least at some of the points of contact between the thermal bonding conjugated staple fibers and main fibers and/or points of contact between the thermal bonding conjugated staple fibers themselves.

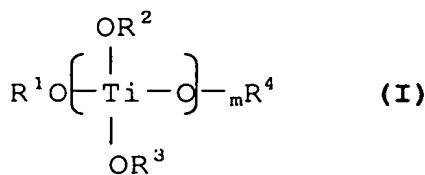
15 The polyester fiber structure of the invention may also be used for purposes which involve contact with food.

20 Best Mode for Carrying Out the Invention
The polyester fiber structure of the invention is formed using a polyester fiber comprising a polyester polymer as the major component.

25 The polyester polymer is produced by polycondensation of an aromatic dicarboxylate ester in the presence of a catalyst. The polycondensation catalyst comprises at least one selected from among (1) mixtures of the titanium compound component (A) and phosphorus compound component (B) described below and (2) reaction products of the titanium compound component (C) and phosphorus compound component (D) described below.

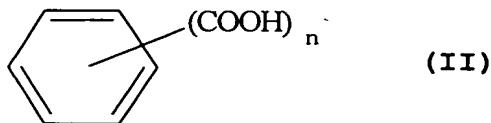
30 The titanium compound (A) of the polycondensation catalyst mixture (1) is composed of at least one compound selected from the group consisting of:

35 (a) titanium alkoxides represented by the following general formula (I):



[wherein R¹, R², R³ and R⁴ each independently represent one species selected from among C₁₋₂₀ and preferably C₁₋₆ alkyl groups and phenyl groups, m represents an integer of 1-4 and preferably 2-4, and when m is an integer of 2, 3 or 4, the two, three or four R² and R³ groups may be the same or different], and

(b) reaction products of titanium alkoxides of general formula (I) above with aromatic polyvalent carboxylic acids represented by the following general formula (II):

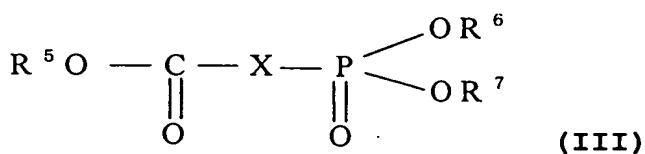


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[wherein n represents an integer of 2-4 and preferably 3-4]

or their anhydrides.

20 The phosphorus compound (B) of the polycondensation catalyst mixture (1) is composed of at least one compound represented by the following general formula (III):



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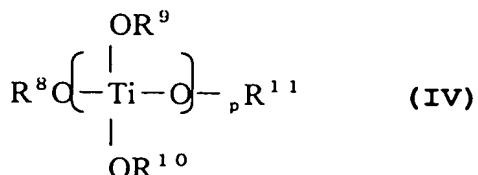
[wherein R⁵, R⁶ and R⁷ each independently represent C₁₋₄ alkyl, and X represents at least one species selected from among -CH₂- and -CH₂(Y) (where Y represents phenyl)].

30 The titanium compound component (C) of the reaction product (2) for the polycondensation catalyst is composed

of at least one compound selected from the group consisting of:

(c) titanium alkoxides represented by the following general formula (IV):

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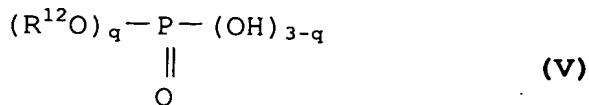


[wherein R^8 , R^9 , R^{10} and R^{11} each independently represent C_{1-20} and preferably C_{1-6} alkyl, p represents an integer of 1-3 and preferably 1-2, and when p is 2 or 3, the two or three R^9 and R^{10} groups may be the same or different], and

10 (d) reaction products of titanium alkoxides of general formula (IV) above with aromatic polyvalent carboxylic acids represented by general formula (II) above or their anhydrides.

15 The phosphorus compound component (D) of the reaction product (2) for the polycondensation catalyst is composed of at least one phosphorus compound represented by the following general formula (V):

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[wherein R^{12} represents C_{1-20} alkyl or C_{6-20} aryl, and q represents an integer of 1 or 2].

25 When a mixture (1) of the titanium compound component (A) and the phosphorus compound component (B) is used as the polycondensation catalyst, the titanium alkoxide (a) represented by general formula (I) or the reaction product (b) of the titanium alkoxide (a) and the aromatic carboxylic acid represented by general formula (II) or its anhydride, used as the titanium compound component (A), have high solubility and compatibility for polyester polymers, and therefore even if residue of the

5 titanium compound component (A) remains in the polyester polymer obtained by polycondensation, there is no accumulation of foreign matter around the spinneret during melt spinning, so that a polyester filament of satisfactory quality can be produced with high spinning efficiency.

10 As titanium alkoxides (a) represented by general formula (I) to be used in the polycondensation catalyst titanium compound component (A) according to the invention, there are preferred tetraisopropoxytitanium, tetrapropoxytitanium, tetra-n-butoxytitanium, tetraethoxytitanium, tetraphenoxytitanium, octaalkyl trititanate and hexaalkyl dititanate.

15 As titanium alkoxides (c) represented by general formula (IV) to be used in the polycondensation catalyst titanium compound component (C) according to the invention, there may be mentioned titanium tetraalkoxides such as titanium tetrabutoxide, titanium tetraisopropoxide, titanium tetrapropoxide and titanium 20 tetraethoxide and alkyl titanates such as octaalkyl trititanate and hexaalkyl dititanate, but titanium tetraalkoxides are preferred for use because of their satisfactory reactivity with the phosphorus compound components used for the invention, and titanium tetrabutoxide is particularly preferred for use.

25 The aromatic polyvalent carboxylic acid of general formula (II) or its anhydride which is reacted with the titanium alkoxide (a) or (c) is preferably selected from among phthalic acid, trimellitic acid, hemimellitic acid, pyromellitic acid, and their anhydrides. In particular, using trimellitic anhydride will yield a reaction product exhibiting high affinity for the polyester polymer, and is effective for preventing accumulation of foreign matter.

35 When the titanium alkoxide (a) or (c) is reacted with the aromatic polyvalent carboxylic acid of general formula (II) or its anhydride, it is preferred, for

example, to dissolve the aromatic polyvalent carboxylic acid or its anhydride in a solvent, add the titanium alkoxide (a) or (c) dropwise to the solution and heat the mixture for at least 30 minutes at a temperature of 0-
5 200°C. The solvent used in this case is preferably selected as desired from among ethanol, ethylene glycol, trimethylene glycol, tetramethylene glycol, benzene and xylene.

There is no particular restriction on the molar ratio for reaction between the titanium alkoxide (a) or (c) with the aromatic polyvalent carboxylic acid of general formula (II) or its anhydride, but if the proportion of the titanium alkoxide is too high, the color tone of the resulting polyester may be impaired or
10 the softening point may be lowered, whereas if the proportion of the titanium alkoxide is too low, the polycondensation reaction may be impeded. The molar ratio for the reaction between the titanium alkoxide (a) or (c) with the aromatic polyvalent carboxylic acid of general formula (II) or its anhydride is therefore
15 preferably in the range of (2:1) to (2:5).

The reaction product (b) or (d) obtained by the reaction may be used directly, or it may be used after purification by recrystallization with acetone, methyl alcohol and/or ethyl acetate.
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The phosphorus compound (phosphonate compound) of general formula (III) to be used for a phosphorus compound component (B) of the polycondensation catalyst mixture (1) according to the invention is preferably selected from among dimethyl esters, diethyl esters, dipropyl esters and dibutyl esters of phosphonic acid derivatives such as carbomethoxymethane-phosphonic acid, carboethoxymethanephosphonic acid, carbopropoxymethanephosphonic acid, carbobutoxymethane-phosphonic acid, carbomethoxyphenylmethanephosphonic acid, carboethoxyphenylmethanephosphonic acid, carbopropoxyphenyl-methanephosphonic acid,
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carbobutoxyphenylmethanephosphonic acid, and the like.

When a phosphorus compound component (B) composed of a phosphorus compound (phosphonate compound) of general formula (III) is used for polycondensation reaction of the aromatic dicarboxylate ester, the reaction with the titanium compound component (A) proceeds more moderately as compared to phosphorus compounds ordinarily used as reaction stabilizers, and therefore the catalytically active life of the titanium compound component (A) during the polycondensation reaction process is longer and as a result, a smaller proportion of the titanium compound component (A) may be used with respect to the amount of the aromatic dicarboxylate ester in the polycondensation reaction system. Also, even if a large amount of stabilizer is added to the polycondensation reaction system containing a phosphorus compound component (B) composed of a phosphorus compound of general formula (III), there is no reduction in thermal stability of the obtained polyester polymer and its color tone is also satisfactory.

When the mixture (1) is used as the polycondensation catalyst according to the invention, the mixture (1) is used with a mixing ratio such that the ratio (%) M_{Ti} of the millimoles of elemental titanium in the titanium compound component (A) with respect to the number of moles of the aromatic dicarboxylate ester and the ratio (%) M_p of the millimoles of elemental phosphorus in the phosphorus compound component (B) with respect to the number of moles of the aromatic dicarboxylate ester satisfy the following relational expressions (i) and (ii):

$$1 \leq M_p/M_{Ti} \leq 15 \quad (i)$$

$$10 \leq M_p+M_{Ti} \leq 100 \quad (ii).$$

The ratio M_p/M_{Ti} is between 1 and 15, and preferably between 2 and 10. If the ratio M_p/M_{Ti} is less than 1, the color tone of the obtained polyester polymer may be yellowish, while if it is greater than 15, the

polycondensation reactivity of the polycondensation catalyst of such a composition will be insufficient, making it difficult to obtain the intended polyester polymer. The range for the ratio M_p/M_{Ti} according to the invention is relatively narrow compared to that for conventional Ti-P catalysts, but establishing such a range produces an excellent effect which has not been obtained with conventional Ti-P catalysts.

The value of the sum (M_p+M_{Ti}) is between 10 and 100, and preferably between 20 and 70. If the value of (M_p+M_{Ti}) is less than 10, the fiber forming property of the obtain polyester polymer, the production efficiency in the melt spinning process and the performance of the obtained fibers will be inadequate. If the value of (M_p+M_{Ti}) is greater than 100, a small but significant degree of foreign matter accumulation will occur around the spinneret when the obtained polyester polymer is used for melt spinning. The value of M_{Ti} is generally preferred to be 2-15% and more preferably 3-10%.

When the reaction product (2) is used as a polycondensation catalyst according to the invention, the phosphorus compound of general formula (V) used as the phosphorus compound (D) may be, for example, a monoalkyl phosphate such as mono-n-butyl phosphate, monohexyl phosphate, monododecyl phosphate, monolauryl phosphate or monooleyl phosphate; a monoaryl phosphate such as monophenyl phosphate, monobenzyl phosphate, mono(4-ethylphenyl) phosphate, monobiphenyl phosphate, mononaphthyl phosphate or monoanthryl phosphate; a dialkyl phosphate such as diethyl phosphate, dipropyl phosphate, dibutyl phosphate, dilauryl phosphate or dioleyl phosphate, or a diaryl phosphate such as diphenyl phosphate. Preferred among these are monoalkyl phosphates or monoaryl phosphates wherein q in formula (V) is 1.

The phosphorus compound component (D) used for the invention may be a mixture of two or more phosphorus

compounds of general formula (V), and as examples of preferred combinations there may be mentioned mixtures of monoalkyl phosphates and dialkyl phosphates or mixtures of monophenyl phosphates and diphenyl phosphates.

5 Particularly preferred are compositions wherein a monoalkyl phosphate constitutes at least 50% and especially at least 90% of the mixture based on the total weight of the mixture.

10 The method of preparing the reaction product of the titanium compound component (C) and phosphorus compound component (D) may involve, for example, combining the components (C) and (D) and heating them in glycol.

15 Specifically, heating a glycol solution containing the titanium compound component (C) and the phosphorus compound component (D) will cause clouding of the glycol solution with precipitation of the components (C) and (D) as reaction products. The precipitate may be collected for use as a catalyst for polyester polymer production.

20 The glycol used in this case is preferably the same glycol component for the polyester to be produced using the obtained catalyst. For example, ethylene glycol is preferred when the polyester is polyethylene terephthalate, 1,3-propanediol is preferred when it is polytrimethylene terephthalate and tetramethylene glycol is preferred when it is polytetramethylene terephthalate.

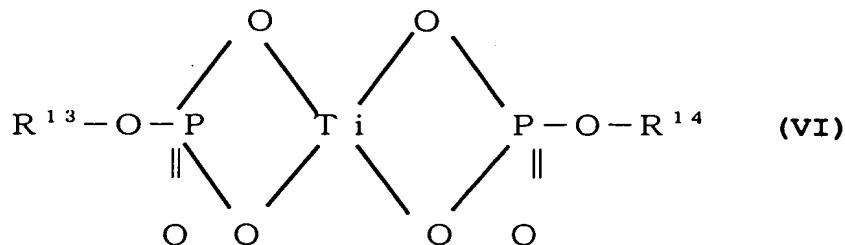
25 The polycondensation reaction product (2) according to the invention may be produced by a method of simultaneously combining the titanium compound component (C) and phosphorus compound (D) and the glycol, and heating them. However, since heating causes the titanium compound component (C) and phosphorus compound component (D) to react and produce a precipitated reaction product which is insoluble in glycol, it is preferred for the reaction up to precipitation to proceed in a uniform manner. In order to efficiently obtain the reaction precipitate, therefore, the preferred production process is one in which separate glycol solutions of the titanium

compound component (C) and phosphorus compound component (D) are prepared beforehand, and the solutions are then combined and heated.

The temperature for the reaction between components (C) and (D) is preferably between 50°C and 200°C, and the reaction time is preferably from 1 minute to 4 hours. If the reaction temperature is too low, the reaction may proceed insufficiently or an excessive reaction time may be required, making it impossible to efficiently obtain a reaction precipitate by uniform reaction.

The mixing proportion of the titanium compound component (C) and phosphorus compound component (D) heated to reaction in glycol is preferably in the range of 1.0 to 3.0 and more preferably 1.5 to 2.5, as the molar ratio of phosphorus atoms with respect to titanium atoms. Within this range, the phosphorus compound component (D) and titanium compound component (C) will react almost completely to avoid the presence of an incomplete reaction product, and therefore the reaction product may be used directly to give a polyester polymer with a satisfactory color tone. In addition, the virtual lack of excess unreacted phosphorus compound (V) results in high productivity without impeding the polyester polymerization reactivity.

The reaction product (2) for the polycondensation catalyst used for the invention preferably comprises a compound represented by the following general formula (VI):



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(wherein R¹³ and R¹⁴ each independently represent at least

one species selected from among C₁₋₁₀ alkyl groups derived from R⁸, R⁹, R¹⁰ and R¹¹ in general formula (IV) representing the titanium alkoxide for titanium compound component (C) and R¹² in general formula (V) representing the phosphorus compound for phosphorus compound component (D), and C₆₋₁₂ aryl groups derived from R¹² in the phosphorus compound (V)).

Since the reaction product of the titanium compound and the phosphorus compound (V) represented by formula (VI) has high catalytic activity, polyester polymers obtained using it have satisfactory color tone (low b value), and exhibit satisfactorily practical polymer performance with a sufficiently low content of acetaldehydes, residual metals and cyclic trimers for practical use. The reaction product represented by formula (VI) is preferably present at 50 wt% or greater and more preferably at 70 wt% or greater.

If the aromatic dicarboxylate ester is subjected to polycondensation in the presence of the reaction product (2), it may be used as a polyester production catalyst directly, without separating the glycol and the precipitated reaction product (2) obtained in the aforementioned manner. Also, after the precipitate has been separated from the glycol solution containing the precipitated reaction product (2) by means such as centrifugal precipitation or filtration, the precipitated reaction product (2) may be recrystallized with, for example, acetone, methyl alcohol and/or water for purification and the purified product used as the catalyst. The structure of the catalyst may be confirmed by solid NMR and XMA metal quantitative analysis.

The polyester polymer used for the invention is obtained by polycondensation of an aromatic dicarboxylate ester in the presence of a catalyst comprising the aforementioned mixture (1) of a titanium compound component (A) and phosphorus compound (phosphonate compound) (B) and/or the reaction product (2) of a

5 titanium compound component (C) and a phosphorus compound component (D). According to the invention, the aromatic dicarboxylate ester is preferably a diester comprising an aromatic dicarboxylic acid component and an aliphatic glycol component.

10 The aromatic dicarboxylic acid is preferably composed mainly of terephthalic acid. More specifically, terephthalic acid preferably constitutes at least 70 mole percent based on the total aromatic dicarboxylic acid component content. As examples of preferred aromatic dicarboxylic acids other than terephthalic acid there may be mentioned phthalic acid, isophthalic acid, naphthalenedicarboxylic acid, diphenyldicarboxylic acid and diphenoxoethanedicarboxylic acid.

15 The aliphatic glycol component is preferably an alkylene glycol, of which there may be used, for example, ethylene glycol, trimethylene glycol, propylene glycol, tetramethylene glycol, neopentyl glycol, hexanemethylene glycol and dodecamethylene glycol, with ethylene glycol being particularly preferred.

20 According to the invention, the polyester polymer is preferably a polyester comprising as its main repeating unit ethylene terephthalate composed of terephthalic acid and ethylene glycol. "Main" means that the ethylene terephthalate repeating unit constitutes at least 70 mole percent of the total repeating units in the polyester.

25 The polyester polymer used for the invention may also be a mixed polyester obtained by copolymerization of polyester components as the acid component or diol component.

30 As mixed carboxylic acid components there may be used the aforementioned aromatic dicarboxylic acids, of course, as well difunctional carboxylic acid components including aliphatic dicarboxylic acids such as adipic acid, sebacic acid, azelaic acid and decanedicarboxylic acid and alicyclic dicarboxylic acids such as cyclohexanedicarboxylic acid, or their ester-forming

derivatives, as starting materials. As mixed diol components there may be used the aforementioned aliphatic diols, of course, as well as alicyclic glycols such as cyclohexanedimethanol and aromatic diols such as
5 bisphenol, hydroquinone and 2,2-bis(4- β -hydroxyethoxyphenyl)propane, as starting materials.

In addition, there may also be used mixed polyester polymers obtained by copolymerization of polyfunctional compounds such as trimesic acid, trimethylolethane,
10 trimethylolpropane, trimethylolmethane and pentaerythritol as mixed components.

Such polyester polymers and mixed polyester polymers may be used alone or in combinations of two or more.

According to the invention, the polyester polymer used is preferably the polycondensation product of an aromatic dicarboxylate ester composed of an aromatic dicarboxylic acid and aliphatic glycol, as described above. The aromatic dicarboxylate ester may also be produced by diesterification reaction of an aromatic dicarboxylic acid and an aliphatic glycol, or it may be produced by transesterification of an aromatic dicarboxylic acid dialkyl ester and an aliphatic glycol.
20 However, methods involving transesterification using dialkyl esters of aromatic dicarboxylic acids as starting materials are more advantageous than methods of diesterification using aromatic dicarboxylic acids as starting materials, because they produce less debris of the phosphorus compound added as a phosphorous stabilizer during the polycondensation reaction.
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Also, all or a portion of the titanium compound component (A) or (C) is preferably added before initiation of the transesterification reaction, for use as a double reaction catalyst, i.e. a transesterification reaction catalyst and polycondensation reaction catalyst.
30 This will allow a reduction in the titanium compound content of the final polyester. More specifically, in the case of polyethylene terephthalate, for example,

transesterification reaction between an aromatic dicarboxylic acid dialkyl ester (composed mainly of terephthalic acid) and ethylene glycol is preferably carried out in the presence of the titanium compound component (A) comprising (a) at least one compound selected from the group consisting of titanium alkoxides represented by general formula (I) above and (b) products of reaction between titanium alkoxides of general formula (I) with aromatic polyvalent carboxylic acids represented by general formula (II) above or their anhydrides. A phosphorus compound (phosphonate compound) represented by general formula (III) above, or the reaction product of a titanium compound component (C) and the aforementioned phosphorus compound component (D), is preferably further added to the reaction mixture comprising the diester of the aromatic dicarboxylic acid and ethylene glycol obtained by the transesterification reaction, and polycondensation reaction is conducted in their presence.

The transesterification reaction will normally be conducted under ordinary pressure, but conducting it under pressurization of 0.05-0.20 MPa will further promote the reaction catalyzed by the action of the titanium compound component (A) while also avoiding bulk generation of diethylene glycol by-product, so that more favorable thermal stability and other properties can be achieved. The temperature is preferably 160-260°C.

When the aromatic dicarboxylic acid used for the invention is terephthalic acid, terephthalic acid and dimethyl terephthalate are used as the starting materials for the polyester. In this case, there may be used recovered dimethyl terephthalate obtained by depolymerization of a polyalkylene terephthalate, or recovered terephthalic acid obtained by hydrolysis thereof. The use of reprocessed polyesters from salvaged PET bottles, fiber products, polyester film products and the like is preferred from the standpoint of effective utilization of resources.

The polycondensation reaction may be carried out in a single tank or in a plurality of separate tanks. The obtained product is a polyester according to the invention, and the polyester obtained by the 5 polycondensation process is usually extruded in a molten state and cooled to form particles (chips).

The polyester used for the invention, which is obtained by the polycondensation process described above, may be further subjected to solid phase polycondensation 10 if desired. The solid phase polycondensation consists of one or more steps and is carried out at a temperature of 190-230°C under a pressure of 1 kPa to 200 kPa in an inert gas atmosphere such as nitrogen, argon or carbon dioxide gas.

15 The particulate polyester obtained from the solid phase polycondensation process is then subjected to water treatment by contact with water, steam, a steam-laden inert gas or steam-laden air as necessary, for inactivation of the catalyst remaining in the chips.

20 The polyester production process described above comprising esterification and polycondensation steps may be carried out in a batch, semi-continuous or continuous system.

25 The polyester polymer used for the invention is preferably selected from among polyethylene terephthalate, polytrimethylene terephthalate and polytetramethylene terephthalate.

30 The polyester polymer used for the invention also preferably has an L* value of 77-85 and a b* value of 2-5 based on the L*a*b* color system (JIS Z8729).

35 The limiting viscosity of the polyester used for the invention obtained in the manner described above is preferably in the range of 0.40-0.80, more preferably 0.45-0.75 and even more preferably 0.50-0.70. The limiting viscosity is preferably not less than 0.40 because the strength of the fibers may be insufficient. On the other hand, a limiting viscosity of greater than

0.80 is uneconomical because it requires excessive raising of the limiting viscosity of the starting polymers.

The polyester used for the invention may, if necessary, contain small amounts of additives such as antioxidants, ultraviolet absorbers, flame retardants, fluorescent brighteners, delustering agents, color correctors, antifoaming agents, antistatic agents, antimicrobial agents, light stabilizers, thermal stabilizers, light blockers or the like, and preferably there are added titanium dioxide as a delustering agent and antioxidants as stabilizers.

The titanium dioxide used preferably has a mean particle size of 0.01-2 μm , and is preferably included in the polyester polymer at 0.01-10 wt%.

Incidentally, the catalyst-derived titanium content in the polyester polymer does not include the titanium derived from any titanium dioxide added as a delustering agent.

When the polyester polymer contains titanium dioxide as a delustering agent, the titanium dioxide of the delustering agent may be removed from the polyester polymer sample for measurement by dissolving the polyester polymer in hexafluoroisopropanol, supplying the solution to centrifugation to separate and precipitate the titanium dioxide particles from the solution, separating and collecting the supernatant liquid by the gradient method and evaporating off the solvent from the collected fraction to prepare the testing sample.

As antioxidants there are preferably used hindered phenol-based antioxidants. An antioxidant is preferably added at no greater than 1 wt% and more preferably 0.005-0.5 wt%. Addition in excess of 1 wt% will result in a saturated effect and may cause scum production during melt spinning. Hindered phenol-based antioxidants may also be used in combination with thioether-based secondary antioxidants.

There are no particular restrictions on the method of adding such antioxidants to the polyester, and they may be added at any desired stage from initiation of the transesterification reaction to completion of the
5 polycondensation reaction.

According to the invention, there are no particular restrictions on the method of producing fibers from the polyester polymer, and any conventional publicly known polyester melt spinning process may be employed. For
10 example, the polyester polymer may be melted and spun in a temperature range of 270-300°C, wherein the melt spinning speed is preferably 400-5000 m/min. A spinning speed within this range will yield fibers with sufficient strength and allow stable winding. Stretching may be
15 carried out after winding the undrawn polyester fibers, or continuously without winding.

The shape of the spinneret used for production of the polyester fiber is also without restrictions and may be circular or irregular in shape (triangular or other polygonal shapes, flat, etc.), and either solid or hollow.
20

There are no restrictions on the form of the polyester fibers used for the invention, and they may be long fibers or staple fibers. The polyester fibers used for the invention may also be twisted or untwisted. In
25 addition, the polyester fibers used for the invention may be subjected to false twisted/crimping, Taslan processing, interlacing, or the like.

The polyester fiber structure of the invention is a
30 fiber structure comprising polyester fiber containing the aforementioned polyester polymer as the major component, and its modes are one or more fiber structures selected from among (1) nonwoven fabrics comprising the polyester fiber, (2) waddings comprising the polyester fiber and
35 (3) fiber structures having thicknesses of 5-100 mm, comprising main fiber made of polyester stable fiber and thermal bonding conjugated staple fiber wherein the

aforementioned polyester polymer is present in either or both the main fiber and the thermal bonding composite stable fiber.

A nonwoven fabric as the first mode of the invention will be explained first. Such a nonwoven fabric is first formed using polyester fiber obtained using at least the aforementioned catalyst, by a dry method (carding method) wherein relatively long staple fibers are opened and mixed using a needle equipped roller, a wet method (sheeting method) wherein relatively short staple fibers are dispersed in water and scraped onto wire, or an airlaid method (also known as airlaying method or dry pulp method) wherein relatively short staple fibers are fed to a perforated drum and dispersed with air to form a web, after which the structure is consolidated by an entanglement/heat treatment step.

Since the optimum conditions will differ depending on the method of producing the nonwoven fabric, these will be explained separately.

20 <Dry methods>

Dry method-produced nonwoven fabrics are characterized by allowing production in a wide range from low basis weight to high basis weight.

When a dry method is applied for the nonwoven fabric, the basis weight is preferably 15-2000 g/m² and more preferably 20-1200 g/m². At less than 15 g/m² it becomes very difficult to continuously produce a uniform web, while at greater than 2000 g/m² the productivity is undesirably poor.

30 The proportion of the polyester fiber used in the nonwoven fabric is not particularly restricted, but from the standpoint of exhibiting an effect on the processing properties it is preferably 50% or greater by weight. In most cases there may also be used, as additional mixed materials, fibers suited for dry nonwoven fabrics (for example, natural fibers such as cotton, semi-synthetic fibers such as rayon and acetate, synthetic fibers such

as PVA fiber, polyolefin fiber, nylon fiber, aramid fiber, acrylic fiber and carbon fiber, or conjugated fibers composed of multiple polymers with different melting points).

5 A suitable fiber consolidating method may be used, such as entanglement of the fibers with a needle (needle punching method), entanglement of the fibers by a high pressure water jet spun lace method), attachment with binder fibers (air-through method), entanglement by
10 shrinkage or pressing with a hot roll.

When a dry method is applied for the nonwoven fabric, the fiber lengths are preferably 30-150 mm and more preferably 5-100 mm. At less than 30 mm the web linkage during fiber opening is weaker and more loss of
15 fiber occurs, while at greater than 150 mm more entanglement tends to occur, resulting in nepping and the like.

When a dry method is applied for the nonwoven fabric, the size of the polyester fiber used is preferably 0.5 dtex to 120 dtex. It is more preferably 1 dtex to 50 dtex. At less than 0.5 dtex the fiber-opening property is poor such that the line speed must be reduced and productivity is greatly impaired, while at greater than 120 dtex it becomes difficult to obtain a uniform
25 web.

The polyester fibers are preferably crimped for application of a dry method for the nonwoven fabric. The crimping method used may be forced crimping, gear crimping, or three-dimensional crimping achieved
30 utilizing anisotropy during spinning.

<Wet methods>

Wet method-produced nonwoven fabrics are characterized by having excellent texture, allowing production of low basis weight fabrics of a few grams, and having high productivity.
35

When a wet method is applied for the nonwoven fabric, the basis weight is preferably 5-200 g/m² and more

preferably 20-100 g/m². At less than 5 g/m² production becomes very difficult, while at greater than 100 g/m² the productivity of the nonwoven fabric is undesirably poor.

5 The proportion of the polyester fiber used in the nonwoven fabric is not particularly restricted, but from the standpoint of exhibiting an effect on the processing properties it is preferably 50% or greater by weight. In most cases there may also be used, as additional mixed materials, fibers suited for wet nonwoven fabrics (for example, natural fibers such as wood pulp and nonwood pulp, semi-synthetic fibers such as rayon and acetate, synthetic fibers such as PVA fiber, polyolefin fiber, nylon fiber, aramid fiber, acrylic fiber and carbon fiber, or conjugated fibers composed of multiple polymers with different melting points).

10 15

The proportion of binder in the wet method-produced nonwoven fabric is preferably in the range of 5-60% and more preferably 10-50% based on weight. At less than 5% a lack of bonding points may result in inadequate strength, while a proportion of greater than 60% results in strong bonding but is undesirable from the standpoint of processing properties such as shrinkage and cohesion during heat treatment.

20

25 The state of the binder is not particularly restricted so long as it is a commonly employed state. A liquid state may even be imparted by internal addition, but a fibrous binder is preferred in consideration of handleability. An example of such a binder is undrawn polyester fiber.

30 When a wet method is applied for the nonwoven fabric, the fiber lengths are preferably 0.1-25 mm and more preferably 3-20 mm. At less than 0.1 mm less entanglement occurs between the fibers making it difficult to achieve a strong nonwoven fabric, while at greater than 25 mm it becomes very difficult to achieve uniform dispersion.

35

When a wet method is applied for the nonwoven

fabric, the size of the polyester fiber used is preferably 0.05 dtex to 10 dtex, and more preferably 0.1 dtex to 7 dtex. At less than 0.05 dtex it becomes difficult to achieve strength, while at greater than 10 dtex it becomes difficult to achieve uniform dispersion.

When a wet method is applied for the nonwoven fabric, there are no particular restrictions on crimping of the polyester fiber used, but in order to bring out bulk there is preferred zigzag mechanical crimping or 10 spiral three-dimensional crimping, or in cases where bulk is not required, they may be straight fibers with no crimping.

When a wet method is applied for the nonwoven fabric, the production process will consist of, largely 15 (1) a sheeting step and (2) a heat treatment step. The sheeting step may employ a short wire paper machine, a cylinder paper machine or the like, or it may be multilayer sheeting with a combination of similar systems or a combination of different systems. The heat treatment step may be accomplished using a rotary dryer, multicylinder dryer, calender or the like, either alone or in combinations depending on the conditions of use. Post-processing such as resin processing or fiber entanglement with a high-pressure jet may also be carried 20 out.

<Airlaid nonwoven fabrics>

Airlaid method-produced nonwoven fabrics have a texture similar to wet method-produced nonwoven fabrics, with a low-density (bulk) structure.

When an airlaid method is applied for the nonwoven fabric, the basis weight is preferably 10-400 g/m² and more preferably 20-300 g/m². A basis weight of less than 10 g/m² renders production very difficult, while a basis weight of greater than 300 g/m² impairs the productivity 30 of the nonwoven fabric.

The proportion of the polyester fiber used in the nonwoven fabric is not particularly restricted, but from

the standpoint of exhibiting an effect on the processing properties it is preferably 50% or greater by weight. In most cases there may also be used, as additional mixed materials, fibers suited for airlaid nonwoven fabrics
5 (for example, natural fibers such as wood pulp and nonwood pulp, semi-synthetic fibers such as rayon and acetate, synthetic fibers such as PVA fiber, polyolefin fiber, nylon fiber, aramid fiber, acrylic fiber and carbon fiber, or conjugated fibers composed of multiple polymers with different melting points).
10

The proportion of binder in the airlaid method-produced nonwoven fabric is preferably in the range of 5-60% and more preferably 10-55% based on weight. At less than 5% a lack of bonding points may result in inadequate strength, while a proportion of greater than 60% results in strong bonding but is undesirable from the standpoint of processing properties such as shrinkage and cohesion during heat treatment. An example of a preferred binder is thermal bonding conjugated staple fiber, described
15 hereunder.
20

When an airlaid method is applied for the nonwoven fabric, the fiber lengths of the polyester fiber used are preferably 1-15 mm and more preferably 3-7 mm. At less than 1 mm less entanglement occurs between the fibers
25 making it difficult to achieve a strong nonwoven fabric, while at greater than 15 mm it becomes very difficult to achieve uniform dispersion.

When an airlaid method is applied for the nonwoven fabric, the size of the polyester fiber used is preferably 0.3 dtex to 100 dtex, and more preferably 1 dtex to 20 dtex. At less than 0.3 dtex it becomes difficult to achieve strength, while at greater than 100 dtex it becomes difficult to achieve uniform dispersion.
30

When an airlaid method is applied for the nonwoven fabric, there are no particular restrictions on crimping of the polyester fiber used, but in order to bring out bulk there is preferred zigzag mechanical crimping or
35

spiral three-dimensional crimping, or in cases where bulk is not required, they may be straight fibers with no crimping.

The production process for an airlaid nonwoven fabric of the invention will consist of, largely (1) a web-forming step and (2) a heat treatment step. The web-forming step may be the well-known process of formation by centrifugal force and suction caused by rotation of two perforated drums (known as "heads") (Dan-Web airlay). By situating multiple heads in series, it is possible to directly produce a nonwoven fabric having stacked layers with different cotton compositions. The heat treatment step may be accomplished by hot air suction treatment, calendering, embossing or the like, either alone or in combinations depending on the conditions of use. Post-processing such as resin processing or fiber entanglement with a high-pressure jet may also be carried out.

The thickness of the nonwoven fabric is preferably between 0.05 mm and 5 mm, whether a wet method, dry method or airlaid method is used.

Wadding as a second embodiment of the invention will now be explained. Wadding preferably consists solely of polyester fiber obtained using the aforementioned catalyst, from the viewpoint of exhibiting an effect on the processing properties. However, other mixed materials may usually be used in combination therewith as necessary, so long as the fibers are suited for production of wadding, such as natural fibers containing no polycondensation catalyst or various synthetic fibers containing no antimony-based catalyst. In such cases as well, however, the proportion of fibers used in combination therewith is preferably no greater than 50% in order to adequately exhibit the effect on the processing properties.

The optimum fiber length of the polyester fibers used in wadding will differ depending on the use to which they are applied, and for example, it is preferably 20-60

mm for blowing-in for stuffed goods or 30-120 mm for purposes requiring production using an ordinary fiber opening machine, such as for futons and resin cotton. In
5 the case of blowing-in, product bulk is difficult to achieve and the bulk durability is poor with lengths of 20 mm and smaller, while the fiber opening property during blow-in is poor and bulk is also difficult to achieve with lengths of 60 mm and larger. For purposes in which the fibers are passed through a fiber opening
10 machine, lengths of 30 mm and smaller result in less entanglement of the fibers and therefore more inconveniences in the steps such as loss of wadding or cuts in the card web, while lengths of 120 mm and larger tend to create problems such as poor fiber opening and
15 poor web ejection.

The size of the polyester fiber used for wadding is preferably 1.0 dtex to 40 dtex and more preferably 3.3 dtex to 20 dtex. At less than 1.0 dtex it is difficult to achieve a product with bulk and the card passage is
20 also impaired, while at greater than 40 dtex the product texture and card passage are impaired.

There are no particular restrictions on the form of crimping of the polyester fiber used for wadding, but in
25 order to bring out greater bulk, coiled three-dimensional crimping is more preferred than zigzag forced crimping. An ordinary process may be used as the method for producing the wadding.

The term "wadding" according to the invention refers to padding used by stuffing opened staple fiber masses directly into cover fabrics, such as for futons or
30 stuffed goods, or resin cotton used as furniture cushion materials, clothing insulation padding and the like, and does not include thermal bonded nonwoven fabrics obtained by mixing and heat treating thermal bonding conjugated fibers, or hard cotton.
35

A third mode of the invention will now be explained, namely, fiber structures having thicknesses of 5-100 mm,

comprising main fiber composed of polyester stable fiber and thermal bonding conjugated staple fiber wherein the polyester polymer is obtained using the aforementioned catalyst in either or both the main fiber and the thermal bonding composite stable fiber.

Such fiber structures are composed of thermal bonding conjugated staple fiber and polyester staple fiber (main fiber), and preferably have thermal anchoring points created by heat treatment at least at some of the 10 points of contact between both fibers and/or points of contact between the thermal bonding conjugated staple fibers themselves.

During this step, the polyester polymer must be comprised in either or both the polyester staple fiber (main fiber) and the thermal bonding conjugated staple fiber.

The aforementioned thermal bonding conjugated staple fiber consists of staple fibers comprising a heat sealing polymer and a fiber-forming thermoplastic polymer with at 20 least the heat sealing polymer exposed on the fiber surfaces.

As heat sealing polymers there may be mentioned polyurethane elastomers, polyester elastomers, inelastic polyester polymers and copolymers, polyolefin polymers and copolymers, and polyvinyl alcohol polymers.

Polyester polymers and their copolymers and polyester elastomers, obtained using the aforementioned catalyst, are preferred.

As copolymerized polyester polymers there may be 30 mentioned copolymer esters comprising prescribed numbers of aliphatic dicarboxylic acids such as adipic acid and sebacic acid, aromatic dicarboxylic acids such as phthalic acid, isophthalic acid and naphthalenedicarboxylic acid and/or alicyclic 35 dicarboxylic acids such as hexahydroterephthalic acid and hexahydroisophthalic acid and aliphatic or alicyclic diols such as diethylene glycol, polyethylene glycol,

propylene glycol and paraxylene glycol, with addition of oxy acids such as parahydroxybenzoic acid as desired, and a preferred example is polyester obtained by addition copolymerization of isophthalic acid and 1,6-hexanediol
5 with terephthalic acid and ethylene glycol.

As examples of polyolefin polymers there may be mentioned low density polyethylene, high density polyethylene, polypropylene and the like.

Examples of fiber-forming thermoplastic polymers to
10 be used in combination with the heat sealing polymer include polyesters such as polyethylene terephthalate, polypropylene terephthalate and polybutylene terephthalate, and polyolefin polymers. The polyester polymers mentioned above obtained using the
15 aforementioned catalyst are particularly preferred.

The combination of the heat sealing polymer and the fiber-forming thermoplastic polymer most preferably employs a polyester-based elastomer with a melting point in the range of 70-210°C (more preferably 100-180°C) as
20 the heat sealing polymer and a polyester polymer with a melting point of 10°C higher than the melting point of the polyester-based elastomer as the fiber-forming thermoplastic polymer.

The thermal bonding conjugated staple fiber is
25 preferably conjugated so that the heat sealing polymer (E) and the fiber-forming thermoplastic polymer (P) are in an area ratio of E:P = 20:80 to 80:20 in the fiber lateral cross-section. The conjugated form of the components (E) and (P) may be any publicly known
30 conjugated form, such as concentric core-sheath, eccentric core-sheath, side-by-side, sea-island conjugated spun fiber or sea-island blended spun fiber, orange section-oriented (split) fiber and the like, but the distribution must be such that a portion of component
35 (E) is exposed on the fiber surfaces, and preferably component (E) constitutes at least 30% of the circumference of the fiber cross-section. Side-by-side

5 or eccentric core-sheath fibers are particularly favorable in that a latent crimping function can be easily imparted for development of minute crimping during heat treatment when the fiber structure is molded, so that entanglement between the fibers can be increased for an enhanced bonding property.

10 The single fiber size of the thermal bonding conjugated staple fiber is preferably in the range of 0.5-200 dtex and more preferably 2-100 dtex. These ranges are preferred in order to result in an optimum number of thermal bonding points formed in the fiber structure by the thermal bonding treatment used to produce the fiber structure, thereby yielding sufficient strength and minimizing agglutination during fabrication 15 of the thermal bonding conjugated staple fiber.

20 The fiber lateral cross-section shapes do not need to be circular and may instead be polygonal, fin-shaped, ball-shaped, etc., although they are preferably circular from the standpoint of forming staple fibers and passing through the carding step. The fibers may also have one or more hollow portions.

The thermal bonding conjugated staple fiber may be produced by a conventional publicly known process.

25 When thermal bonding conjugated fiber is cut into staple fiber, the cut lengths are preferably in the range of 5-100 mm and particularly in the range of 15-95 mm. This range yields especially favorable carding properties and fiber structure bonding properties.

30 The thermal bonding conjugated staple fiber may also be crimped so long as it produces no problems during the process, and in such case the number of crimps is preferably in the range of 8-20 per 25 mm, with a crimping ratio in the range of 6-18%.

35 The polyester staple fiber used as the main fiber may be composed of a publicly known polyester, but it is preferably composed of the aforementioned polyester polymer obtained using the catalyst described above. The

single fiber size of the polyester staple fiber is preferably in the range of 0.5-150 dtex and more preferably 2-50 dtex from the standpoint of the fiber structure bulk, cushion property and resilience, as well
5 as texture. From the standpoint of the fiber structure bulk and cushion property, the number of crimps in the polyester staple fiber is preferably in the range of 3-30 per 25 mm and more preferably in the range of 5-20 per 25 mm, and the crimping ratio is preferably in the range of
10 6-50% and more preferably in the range of 12-40%. The cut lengths are preferably in the range of 5-100 mm and especially in the range of 15-90 mm.

The cross-sectional shapes of the polyester staple fibers are preferably circular, flat, triangular,
15 hexagonal or hollow, as appropriately selected according to the intended use.

The polyester staple fiber may be produced by employing a conventional publicly known process for reeling or drafting of fiber composed of a single
20 component or conjugated fiber obtained by conjugation of two or more components.

The blending proportion of both of the staple fibers of the aforementioned fiber structure according to the third mode of the invention is preferably in the range of thermal bonding conjugated staple fiber:polyester staple
25 fiber = 5:95 to 70:30 and more preferably 10:90 to 60:40, based on weight. If the blending proportion of the thermal bonding conjugated staple fiber is too high, too many thermal anchoring points formed in the fiber
30 structure may result in excessive hardness of the structure, while if it is too low, too few thermal anchoring points may result in inferior elasticity and durability of the structure.

The thickness of the fiber structure must be in the range of 5-100 mm. The density is appropriately in the range of 0.01-0.10 g/cm³.

The process for fabricating the fiber structure may

be any publicly known process so long as it allows formation of thermal anchoring points at least at some of the points of contact between the thermal bonding conjugated staple fibers and polyester staple fibers 5 and/or points of contact between the thermal bonding conjugated staple fibers themselves.

The heat treatment temperature is preferably about 100-215°C and the heat treatment time is preferably about 10-30 minutes.

10

Examples

15

The present invention will now be further explained by the following examples, with the understanding that the examples are not limitative on the scope of the invention.

20

For Examples 1-21 and Comparative Examples 1-12, the limiting viscosity, color tone, metal content, nonwoven fabric strength/elongation, nonwoven fabric quality variation, generation of waste cotton during fiber opening, wadding quality variation, fiber structure hardness (elasticity), residual deformation of fiber structure with repeated compression (durability), hard masses in the fiber structure, fiber structure thickness, fiber structure density and spinneret adhesion for each 25 of the polyester polymers were measured by the methods described below.

25

(1) Limiting viscosity:

30

Calculated after heating 0.6 g of polyester to dissolution in 50 cc of o-chlorophenol, cooling the solution and using an Ostwald viscosity tube for measurement of the solution viscosity according to an ordinary method at a temperature of 35°C.

(2) Color tone (color L value/color b value):

35

Measured with a CM-7500 Color Machine by Color Machines Co. after heat treatment of the particulate polymer sample in a dryer at 160°C x 90 min and

recrystallization.

(3) Metal content:

For the titanium atom content and phosphorus atom content of the catalyst system as a catalyst solution, the catalyst solution was filled into a liquid cell, while for the polyester polymer, the polyester polymer sample was heated to melting on an aluminum plate and then supplied to a compression press and formed into a level molded article. The sample was supplied to a fluorescent X-ray analyzer (Model 3270 by Rigaku Corp.) for quantitative analysis of the metal content.

(4) Nonwoven fabric strength/elongation:

A constant-speed ductile tensile tester was used for measurement according to the method of JIS P8113.

(5) Nonwoven fabric quality variation:

The quality variation was based on the standard deviation per n=30 for the tensile strength of the nonwoven fabric. (A smaller value indicates lower variation and thus greater quality stability.)

(6) Generation of waste cotton during fiber opening:

The weight of waste cotton generated per hour under ordinary roller carding conditions for futon wadding production was measured in a 1 m² region around the carding machine.

(7) Wadding quality variation:

The quality variation was based on the standard deviation per n=10 for measurement of weight of waste cotton generated per hour. (A smaller value indicates lower variation and thus greater quality stability.)

(8) Fiber structure hardness (elasticity):

This was measured based on the 25% compression hardness according to JIS-K6401.

(9) Residual deformation of fiber structure with repeated compression (durability):

This was measured according to the method of JIS-K6401.

(10) Hard masses in fiber structure:

Ten specialists were randomly selected for hand contact with the surface of the fiber structure, and the condition of hard masses was organoleptically evaluated on the following scale.

5 5: Very satisfactory (very uniform with no discernible masses)

 4: Somewhat satisfactory (mostly uniform with virtually no masses)

 3: Satisfactory (partial masses but not significant)

10 2: Somewhat poor (discernible masses)

 1: Very poor (definitely large number of masses)

(11) Fiber structure thickness:

The thickness (mm) was measured according to JISL1096.

15 (12) Fiber structure density:

The density (g/cm³) was measured according to JISL1097.

(13) Diethylene glycol (DEG) content:

20 Hydrazine hydrate was used for decomposition of the polymer, and gas chromatography (Model 263-70 by Hitachi Laboratories) was used for measurement according to a common method.

(14) Adhesion layer produced on spinneret:

25 The polyester was prepared into chips, melted at 290°C, and then discharged from a spinneret having 12 holes each with a hole size of 0.15 mmφ for spinning at a speed of 600 m/min for 2 days, after which the height of the adhesion layer produced on the outer rim of the discharge port of the mouthpiece was measured. A greater height of the adhesion layer tends to result in more bending of the filament current of the discharged polyester melt, and thus lowers the moldability of the polyester. That is, the height of the adhesion layer produced on the spinneret was used as an index of the moldability of the polyester.

Example 1

After charging 0.009 part of tetra-n-butyl titanate into a mixture of 100 parts of dimethyl terephthalate and 70 parts of ethylene glycol in a pressure reaction-capable stainless steel reactor, pressurization was conducted at 0.07 MPa for transesterification reaction while increasing the temperature from 140°C to 240°C, and then 0.04 part of triethyl phosphonoacetate was added to terminate the transesterification reaction.

The reaction product was then transferred to a polymerization reactor, the temperature was raised to 290°C, and polycondensation reaction was conducted in a high vacuum of no greater than 26.67 Pa to obtain a (delustering agent-free) polyester with a limiting viscosity of 0.60, a diethylene glycol content of 1.5 wt% and a melting point of 254°C.

The obtained polyester was prepared into chips and dried by ordinary procedures. The dried chips were used for spinning, stretching, cutting, etc. according to ordinary methods to obtain polyester drawn yarn (size: 1.7 dtex, fiber length: 5 mm, crimps: 0) and polyester undrawn yarn as a binder (size: 1.2 dtex, fiber length: 5 mm, crimps: 0). The polyester drawn yarn and polyester undrawn yarn were mixed in a proportion of 60/40 and sheeted to a basis weight of 50 g/m² using an ordinary cylinder paper machine, and then dried with a Yankee dryer and further subjected to calender treatment. The properties of the obtained wet nonwoven fabric are shown in Table 1.

Reference Example

Titanium trimellitate synthesis method:

Tetrabutoxytitanium was added to a solution of trimellitic anhydride in ethylene glycol (0.2%) at 1/2 mole with respect to the trimellitic anhydride, and reaction was conducted for 60 minutes in air at normal pressure while maintaining a temperature of 80°C, after

which the system was cooled to ordinary temperature and the produced catalyst was recrystallized with a 10-fold amount of acetone, and then the precipitate was filtered out with filter paper and dried at 100°C for 2 hours to obtain the target compound.

5

Example 2

The same procedure was carried out as in Example 1, except that 0.016 part of titanium trimellitate synthesized by the method described in the reference 10 example was used as the titanium compound. The results are shown in Table 1.

10

Examples 3-5, Comparative Examples 1-3

The same procedure was carried out as in Example 1, except for adding the titanium compounds and phosphorus 15 compounds listed in Table 1 in the indicated amounts. The results are shown in Table 1.

15

Example 6

The polyester chips obtained in Example 1 were used 20 for spinning, stretching, cutting, etc. according to ordinary methods to obtain polyester drawn yarn (size: 1.7 dtex, fiber length: 51 mm, crimps: 12/inch). The polyester drawn yarn was formed into a web with a basis weight of 100 g/m² using an ordinary roller carding machine, and then a needle punch machine was used to 25 entangle the fibers to obtain a dry nonwoven fabric. The properties thereof are shown in Table 1.

25

Example 7

Spinning, stretching, cutting, etc. were carried out 30 according to ordinary methods, using the polyester chips obtained in Example 1 as a core component and chips consisting of a copolymer polyester comprising an acid component obtained by mixing terephthalic acid and isophthalic acid at 60/40 (mole percent) and a diol component obtained by blending ethylene glycol and 1,6-35 hexanediol at 85/15 (mole percent) (limiting viscosity: 0.36, softening point: 70°C), prepared using a similar catalyst, as a sheath component to obtain core-sheath

30

35

conjugated polyester fiber (core/sheath ratio: 50/50, size: 2.2 dtex, fiber length: 5 mm). The core-sheath conjugated polyester fiber was blended with beaten wood pulp in a proportion of 60/40 and used for 50 g/m² web formation with an airlaid machine, and then subjected to heat treatment with an air-through dryer. The properties of the obtained airlaid nonwoven fabric are shown in Table 1.

Comparative Example 4

After charging 0.064 part by weight of calcium acetate monohydrate into a mixture of 100 parts of dimethyl terephthalate and 70 parts of ethylene glycol in a pressure reaction-capable stainless steel reactor, pressurization was conducted at 0.07 MPa for transesterification reaction while increasing the temperature from 140°C to 240°C, and then 0.044 part of a 56 wt% aqueous phosphoric acid solution was added to terminate the transesterification reaction.

The reaction product was then transferred to a polymerization reactor, diantimony trioxide was added in the amount shown in the table, the temperature was raised to 290°C, and polycondensation reaction was conducted in a high vacuum of no greater than 26.67 Pa to obtain a polyester. The obtained polyester was made into fiber and then used to obtain a nonwoven fabric, in the same manner as Example 1. The results are shown in Table 1.

Table 1

	Titanium compound Type Content (mmol%)	Phosphorus compound Type Content (mmol%)	Sb compound (Sb ₂ O ₃) (mmol%)	P/Ti (mmol%)	Ti+P (mmol%)	Limiting viscosity value	L value	b value	Method length (km)	Breaking length (km)	Elongation (%)	Color	Nonwoven fabric properties
Example 1	TBT 5	TEPA 30	-	6	35	0.620	79.0	3.0	wet	0.12	1.5	0.06	
Example 2	TMT 5	TEPA 30	-	6	35	0.620	80.0	2.8	wet	0.13	1.6	0.04	
Example 3	TMT 5	PEE 30	-	6	35	0.620	78.0	3.0	wet	0.11	1.5	0.05	
Example 4	TMT 3	TEPA 15	-	5	18	0.600	80.0	2.3	wet	0.12	1.7	0.06	
Example 5	TMT 7	TEPA 50	-	7	57	0.600	80.0	3.3	wet	0.13	1.9	0.05	
Example 6	TBT 5	TEPA 30	-	6	35	0.620	79.0	3.0	dry	1.21	89.1	0.11	
Example 7	TBT 5	TEPA 30	-	6	35	0.620	79.0	3.0	airlaid	0.45	22.1	0.09	
Comp.Ex.1	TMT 5	TEPA 90	-	18	95	0.520	83.0	0.0	wet	0.13	1.9	0.3	
Comp.Ex.2	TMT 9	TEPA 100	-	11.1	109	0.600	78.0	3.0	wet	0.11	2.4	0.3	
Comp.Ex.3	TMT 2	TEPA 7	-	3.5	9	0.600	80.0	2.0	wet	0.12	2.1	0.2	
Comp.Ex.4	-	-	-	31	-	0.620	78.0	3.0	wet	0.13	2.3	0.3	

TBT: tetra-n-butoxytitanium

TMT: titanium trimellitate

TEPA: triethyl phosphonoacetate

PEE: carboethoxymethane-phosphonic acid diethyl ester

Example 8

The same polyethylene terephthalate chips as in Example 1 were dried. The dried chips were used for spinning, stretching, cutting, etc. according to ordinary methods to obtain polyester drawn yarn (size: 6.6 dtex, fiber length: 51 mm, coiled three-dimensional crimps: 9.0/25 mm). The polyester drawn yarn was opened with an ordinary roller carding machine and formed into a futon card web. The waste cotton generated is shown in Table 2.

Example 9

The same procedure was carried out as in Example 8, except that 0.016 part of titanium trimellitate synthesized by the method described in the reference example was used as the titanium compound. The results are shown in Table 2.

Examples 10-14, Comparative Examples 5-7

The same procedure was carried out as in Example 8, except for adding the titanium compounds and phosphorus compounds listed in Table 2 in the indicated amounts. The results are shown in Table 2.

Comparative Example 8

After charging 0.064 part by weight of calcium acetate monohydrate into a mixture of 100 parts of dimethyl terephthalate and 70 parts of ethylene glycol in a pressure reaction-capable stainless steel reactor, pressurization was conducted at 0.07 MPa for transesterification reaction while increasing the temperature from 140°C to 240°C, and then 0.044 part of a 56 wt% aqueous phosphoric acid solution was added to terminate the transesterification reaction.

The reaction product was then transferred to a polymerization reactor, diantimony trioxide was added in the amount shown in the table, the temperature was raised to 290°C, and polycondensation reaction was conducted in a high vacuum of no greater than 26.67 Pa to obtain a polyester. The obtained polyester was made into fiber

and then used to obtain wadding, in the same manner as Example 8. The results are shown in Table 2.

Table 2

	Titanium compound		Phosphorus compound		Sb compound (Sb ₂ O ₃) (mmol%)	P/Ti (mmol%)	Ti+P (mmol%)	Limiting viscosity value (mmol%)	Color value L value	Filament properties		Wadding processing properties						
	Type	Content (mmol%)	Type	Content (mmol%)						Filament properties		Wadding processing properties						
										b value	Strength CN/dtex	Elongation %	Mean waste cotton (g)	Quality variation				
Example 8	TBT	5	TEPA	30	—	6	35	0.620	79.0	3.0	3.7	27	8	0.07				
Example 9	TMT	5	TEPA	30	—	6	35	0.620	80.0	2.8	3.8	26	11	0.06				
Example 10	TMT	5	PEE	30	—	6	35	0.620	78.0	3.0	3.6	28	12	0.06				
Example 11	TMT	3	TEPA	15	—	5	18	0.600	80.0	2.3	3.7	27	6	0.03				
Example 12	TMT	7	TEPA	50	—	7	57	0.600	80.0	3.3	3.6	25	11	0.12				
Example 13	TMT	5	TMP	30	—	6	35	0.600	77.0	4.0	3.6	26	9	0.11				
Example 14	titanium acetate	5	TEPA	30	—	6	35	0.600	78.0	4.5	3.6	29	13	0.10				
Comp.Ex. 5	TMT	5	TEPA	90	—	18	95	0.520	83.0	0.0	3.2	22	12	0.18				
Comp.Ex. 6	TMT	9	TEPA	100	—	11.1	109	0.600	78.0	3.0	3.7	29	11	0.26				
Comp.Ex. 7	TMT	2	TEPA	7	—	3.5	9	0.600	80.0	2.0	3.6	27	15	0.22				
Comp.Ex. 8	—	—	—	—	—	31	—	0.620	78.0	3.0	3.9	28	55	0.42				

TBT: tetra-n-butoxytitanium

TMT: titanium trimellitate

TEPA: triethyl phosphonoacetate

PEE: carboethoxymethane-phosphonic acid diethyl ester

TMP: trimethyl phosphate

Example 15

The same polyethylene terephthalate chips as in Example 1 were dried and used to obtain polyester staple fibers with a single fiber size of 12 dtex, 8 crimps/25 mm and a crimping ratio of 30% by an established method. The same chips were also used as the core component, while the same catalyst was used for polymerization of a mixed acid component comprising terephthalic acid and isophthalic acid at 80/20 (mole percent) and butylene glycol, and the obtained polybutylene-based terephthalate was further subjected to heated reaction at 38 wt% with 62 wt% of polybutylene glycol (molecular weight: 2000), to obtain a block copolymer polyether-ester elastomer (thermoplastic elastomer) with a limiting viscosity of 1.0 and a melting point of 155°C. The obtained thermoplastic elastomer was used as the sheath component, and spinning, stretching, cutting, etc. were carried out for a fiber cross-sectional area core/sheath ratio of 60/40, to obtain a thermal bonding conjugated staple fiber (core/sheath ratio: 60/40, fiber size: 6 dtex, 11 crimps/25 mm, crimping ratio: 8%).

The polyester staple fiber and thermal bonding conjugated staple fiber were mixed in a weight proportion of 70:30 and passed twice through a roller carding machine to obtain a blended web. The web was placed in a molding frame at a fixed density and subjected to heat treatment at 180°C x 15 min using a circulating hot air dryer to obtain a fiber structure with a density of 0.04 g/cm³ and a thickness of 5 cm. The properties of the obtained fiber structure were evaluated and the results are shown in Table 3.

Example 16

The same procedure was carried out as in Example 15 to obtain a fiber structure, except that 0.016 part of titanium trimellitate synthesized by the method described in the reference example was used as the titanium compound. The results are shown in Table 3.

Examples 17-21, Comparative Examples 9-11

The same procedure was carried out as in Example 15 to obtain a fiber structure, except for adding the titanium compounds and phosphorus compounds listed in 5 Table 3 in the indicated amounts. The results are shown in Table 3.

Comparative Example 12

After charging 0.064 part by weight of calcium acetate monohydrate into a mixture of 100 parts of 10 dimethyl terephthalate and 70 parts of ethylene glycol in a pressure reaction-capable stainless steel reactor, pressurization was conducted at 0.07 MPa for transesterification reaction while increasing the temperature from 140°C to 240°C, and then 0.044 part of a 15 56 wt% aqueous phosphoric acid solution was added to terminate the transesterification reaction.

The reaction product was then transferred to a polymerization reactor, diantimony trioxide was added in the amount shown in the table, the temperature was raised 20 to 290°C, and polycondensation reaction was conducted in a high vacuum of no greater than 26.67 Pa to obtain a polyester. The obtained polyester was made into fiber and then used to obtain a fiber structure, in the same manner as Example 15. The results are shown in Table 3.

Table 3

	Titanium compound		Phosphorus compound		Sb compound Sb ₂ O ₃ mmol%	P/Ti mmol%	Ti+P mmol%	Limiting viscosity mmol%	Color		Filament properties		Fiber structure quality						
	Type	Content mmol%	Type	Content mmol%					L value	b value	CN/dtex	Elongation %	Hardness N	Residual deformation with repeated compression %	Hard masses				
Example 15	TBT	5	TEPA	30	-	6	35	0.620	79.0	3.0	3.7	27	370	8.8	5				
Example 16	TMT	5	TEPA	30	-	6	35	0.620	80.0	2.8	3.8	26	380	7.1	5				
Example 17	TMT	5	PEE	30	-	6	35	0.620	78.0	3.0	3.8	28	385	8.4	5				
Example 18	TMT	3	TEPA	15	-	5	18	0.600	80.0	2.3	3.6	27	360	10.2	5				
Example 19	TMT	7	TEPA	50	-	7	57	0.600	80.0	3.3	3.7	25	374	9.3	5				
Example 20	TMT	5	TMP	30	-	6	35	0.600	77.0	4.0	3.6	26	363	11.3	5				
Example 21	titanium acetate	5	TEPA	30	-	6	35	0.600	78.0	4.5	3.6	29	360	10.9	5				
Comp.Ex.9	TMT	5	TEPA	90	-	18	95	0.520	83.0	0.0	3.2	22	340	14.0	2				
Comp.Ex.10	TMT	9	TEPA	100	-	11.1	109	0.600	78.0	3.0	3.7	29	378	9.0	3				
Comp.Ex.11	TMT	2	TEPA	7	-	3.5	9	0.600	80.0	2.0	3.6	27	358	11.0	3				
Comp.Ex.12	-	-	-	-	31	-	-	0.620	78.0	3.0	3.9	28	415	7.0	3				

TBT: tetra-n-butoxytitanium, TMT: titanium trimellitate, TEPA: triethyl phosphonoacetate, PEE: carboethoxymethane-phosphonic acid diethyl ester, TMP: trimethyl phosphate

For Examples 22-36 and Comparative Examples 13-23, the limiting viscosity, color tone, metal content, nonwoven fabric strength/elongation, nonwoven fabric quality variation, generation of waste cotton during fiber opening, wadding quality variation, fiber structure hardness (elasticity), residual deformation of fiber structure with repeated compression (durability), hard masses in the fiber structure, fiber structure thickness, fiber structure density and spinneret adhesion for each of the polyester polymers were measured by the methods described below.

(1) Limiting viscosity:

Calculated after heating 0.6 g of polyester to dissolution in 50 cc of o-chlorophenol, cooling the solution and using an Ostwald viscosity tube for measurement of the solution viscosity according to an ordinary method at a temperature of 35°C.

(2) Color tone (color L value/color b value):

Measured with a CM-7500 Color Machine by Color Machines Co. after heat treatment of the particulate polymer sample in a dryer at 160°C x 90 min and recrystallization.

(3) Analysis of metal contents:

The titanium and phosphorus atom concentrations of the reaction precipitated catalyst were quantitatively analyzed by setting the dried sample in a scanning electron microscope (SEM, S570 by Hitachi Instruments Service) and using an energy dispersive X-ray microanalyzer (XMA, EMAX-7000 by Horiba Co., Ltd.) connected to it.

The catalyst metal concentration in the polyester was quantitatively analyzed by heating the particulate sample to melting on an aluminum plate and then forming a level molded article thereof with a compression press and using a fluorescent X-ray analyzer (Model 3270 by Rigaku Corp.).

(4) Nonwoven fabric strength/elongation:

A constant-speed ductile tensile tester was used for measurement according to the method of JIS P8113.

(5) Nonwoven fabric quality variation:

The quality variation was based on the standard deviation per n=30 for the tensile strength of the nonwoven fabric. (A smaller value indicates lower variation and thus greater quality stability.)

(6) Generation of waste cotton during fiber opening:

The weight of waste cotton generated per hour under ordinary roller carding conditions for futon wadding production was measured in a 1 m² region around the carding machine.

(7) Wadding quality variation:

The quality variation was based on the standard deviation per n=10 for measurement of weight of waste cotton generated per hour. (A smaller value indicates lower variation and thus greater quality stability.)

(8) Fiber structure hardness (elasticity):

This was measured based on the 25% compression hardness according to JIS-K6401.

(9) Residual deformation of fiber structure with repeated compression (durability):

This was measured according to the method of JIS-K6401.

(10) Hard masses in fiber structure:

Ten specialists were randomly selected for hand contact with the surface of the fiber structure, and the condition of hard masses was organoleptically evaluated on the following scale.

30 5: Very satisfactory (very uniform with no discernible masses).

4: Somewhat satisfactory (mostly uniform with virtually no masses)

3: Satisfactory (partial masses but not significant)

35 2: Somewhat poor (discernible masses)

1: Very poor (definitely large number of masses)

(11) Fiber structure thickness:

The thickness (mm) was measured according to JISL1096.

(12) Fiber structure density:

The density (g/cm^3) was measured according to 5 JISL1097.

(13) Adhesion layer produced on spinneret:

The polyester was prepared into chips, melted at 10 290°C , and then discharged from a spinneret having 12 holes each with a hole size of $0.15 \text{ mm}\phi$ for spinning at a speed of $600 \text{ m}/\text{min}$ for 2 days, after which the height of the adhesion layer produced on the outer rim of the discharge port of the mouthpiece was measured. A greater height of the adhesion layer tends to result in more bending of the filament current of the discharged 15 polyester melt, and thus lowers the moldability of the polyester. That is, the height of the adhesion layer produced on the spinneret was used as an index of the moldability of the polyester.

20 Example 22

Preparation of titanium compound:

A 2 L three-necked flask equipped with a function allowing mixing and stirring of the contents was prepared, 919 g of ethylene glycol and 10 g of acetic acid were placed therein, and after stirring and mixing, 25 71 g of titanium tetrabutoxide was slowly added to obtain a (transparent) solution of a titanium compound in ethylene glycol. This solution will hereinafter be abbreviated as "TB solution". The titanium atom concentration of the solution was 1.02%.

Preparation of phosphorus compound:

A 2 L three-necked flask equipped with a function allowing heating, mixing and stirring of the contents was prepared, and 656 g of ethylene glycol was placed therein 35 and heated to 100°C while stirring. Upon reaching 100°C , 34.5 g of monolauryl phosphate was added, and the mixture

was heated, mixed and stirred to dissolution to obtain a transparent solution. This solution will hereinafter be abbreviated as "P1 solution".

Preparation of catalyst:

5 Next, 310 g of the prepared TB solution was slowly added to the P1 solution (approximately 690 g) under heating control at 100°C and stirring, and upon addition of the entire amount, stirring was continued for 1 hour at a temperature of 100°C to complete reaction of the
10 titanium compound and phosphorus compound. The mixing ratio of the TB solution and P1 solution was 2.0 as the molar ratio of phosphorus atoms with respect to titanium atoms. The product obtained by the reaction was insoluble in ethylene glycol and was therefore present as
15 a turbid, fine precipitate. This solution will hereinafter be abbreviated as "TP1-2.0 catalyst".

In order to analyze the obtained reaction precipitate, a portion of the reaction solution was filtered with a 5 μ pore filter to obtain the
20 precipitated reaction product as a solid, and it was then washed with water and dried. The elemental concentration of the obtained precipitated reaction product was analyzed by XMA, yielding results of 12.0% titanium, 16.4% phosphorus and a phosphorus atom molar ratio of 2.1
25 with respect to titanium atoms. Solid NMR analysis yielded the following results. C-13 CP/MAS (75.5 Hz frequency) measurement revealed disappearance the butoxide-derived chemical shift peaks at 14 ppm, 20 ppm and 36 ppm for titanium tetrabutoxide, while P-31 DD/MAS (121.5 Hz frequency) measurement confirmed a new chemical shift peak at 22 ppm not found in conventional monolauryl phosphate. These data clearly indicated that the precipitate obtained under these conditions was a new compound resulting from reaction of the titanium compound
30 and phosphorus compound.

35 Separately, a slurry prepared by mixing 179 parts of

high purity terephthalic acid and 95 parts of ethylene glycol was supplied at a constant rate to a reactor already holding 225 parts of an oligomer (oligomer of an ethylene glycol terephthalate diester) while stirring in 5 a nitrogen atmosphere under conditions kept at 255°C, ordinary pressure, and esterification reaction was carried out for 4 hours to completion while removing out of the system the water and ethylene glycol generated by the reaction. The esterification rate was >98% and the 10 polymerization degree of the produced oligomer was about 5-7.

After transferring 225 parts of the oligomer obtained by the esterification reaction to a polycondensation reactor, 3.34 parts of the "TP1-2.0 15 catalyst" produced earlier was charged in as the polycondensation catalyst. The reaction temperature in the system was raised from 255°C to 280°C and the reaction pressure lowered from atmospheric pressure to 60 Pa in stages, for polycondensation reaction while removing out 20 of the system the water and ethylene glycol generated by the reaction.

The extent of the polycondensation reaction was confirmed while monitoring the load on the stirring blade in the system, and the reaction was suspended when the 25 desired degree of polymerization was reached. The reaction product in the system was then continuously extruded into a strand from the discharge port and then cooled and cut to obtain granular pellets of approximately 3 mm. The quality of the obtained 30 polyethylene terephthalate is shown in Table 4.

The chips were dried and used for spinning, stretching, cutting, etc. according to ordinary methods to obtain polyester drawn yarn (size: 1.7 dtex, fiber length: 5 mm, crimps: 0) and polyester undrawn yarn as a 35 binder (size: 1.2 dtex, fiber length: 5 mm, crimps: 0). The polyester drawn yarn and polyester undrawn yarn were mixed in a proportion of 60/40 and sheeted to a basis

weight of 50 g/m² using an ordinary cylinder paper machine, and then dried with a Yankee dryer and further subjected to calender treatment. The properties of the obtained wet nonwoven fabric are shown in Table 4.

5

Example 23

The same procedure was carried out as in Example 22, except that monobutyl phosphate was used instead of monolauryl phosphate. The addition amount and conditions were also changed in the following manner.

10

After heating and dissolving 28.3 g of monobutyl phosphate in 537 g of ethylene glycol (hereinafter abbreviated as "P2 solution"), 435 g of TB solution was placed therein and a reaction product was obtained. The mixing ratio of the TB solution and P2 solution was 2.0 as the molar ratio of phosphorus atoms with respect to titanium atoms. This solution will hereinafter be abbreviated as "TP2-2.0 catalyst". The heating temperature was 70°C and the reaction time was 1 hour.

15

In order to analyze the obtained reaction precipitate, a portion of the reaction solution was filtered with a 5 μ pore filter to obtain the precipitated reaction product as a solid, and it was then washed with water and dried. The elemental concentration of the obtained precipitated reaction product was analyzed in the same manner as above, yielding results of 17.0% titanium, 21.2% phosphorus and a phosphorus atom molar ratio of 1.9 with respect to titanium atoms. The catalyst was used for production of polyester fiber in the same manner as Example 1, after which sheeting and drying were carried out to obtain a wet nonwoven fabric. The results are shown in Table 4.

20

Example 24

The same procedure was carried out as in Example 22, except that the amount of TP1 solution prepared and the 35 amount of TB solution added were changed. The amounts prepared and added were as follows.

After heating and dissolving 31.3 g of monolauryl

phosphate in 594 g of ethylene glycol (hereinafter abbreviated as "P3 solution"), 375 g of TB solution was placed therein and a reaction product was obtained. The mixing ratio of the TB solution and P3 solution was 1.5 as the molar ratio of phosphorus atoms with respect to titanium atoms. This solution will hereinafter be abbreviated as "TP3-1.5 catalyst". The catalyst was used for production of polyester fiber in the same manner as Example 22, after which sheeting and drying were carried out to obtain a wet nonwoven fabric. The results are shown in Table 4.

Example 25

The same procedure was carried out as in Example 23, except that the amount of TP2 solution prepared and the amount of TB solution added were changed. The amounts prepared and added were as follows.

After heating and dissolving 33.0 g of monobutyl phosphate in 627 g of ethylene glycol (hereinafter abbreviated as "P4 solution"), 340 g of TB solution was placed therein and a reaction product was obtained. The mixing ratio of the TB solution and P4 solution was 3.0 as the molar ratio of phosphorus atoms with respect to titanium atoms. This solution will hereinafter be abbreviated as "TP4-3.0 catalyst". The catalyst was used for production of polyester fiber in the same manner as Example 22, after which sheeting and drying were carried out to obtain a wet nonwoven fabric. The results are shown in Table 4.

Example 26

The polyester chips obtained in Example 22 were used for spinning, stretching, cutting, etc. according to ordinary methods to obtain polyester drawn yarn (size: 1.7 dtex, fiber length: 51 mm, crimps: 12/inch). The polyester drawn yarn was formed into a web with a basis weight of 100 g/m² using an ordinary roller carding machine, and then a needle punch machine was used to entangle the fibers to obtain a dry nonwoven fabric. The

properties thereof are shown in Table 4.

Example 27

Spinning, stretching, cutting, etc. were carried out according to ordinary methods, using the polyester chips obtained in Example 22 as a core component and chips consisting of a copolymer polyester comprising an acid component obtained by mixing terephthalic acid and isophthalic acid at 60/40 (mole percent) and a diol component obtained by mixing ethylene glycol and 1,6-hexanediol at 85/15 (mole percent) (limiting viscosity: 0.36, softening point: 70°C), prepared using a similar catalyst, as a sheath component to obtain core-sheath conjugated polyester fiber (core/sheath ratio: 50/50, size: 2.2 dtex, fiber length: 5 mm). The core-sheath conjugated polyester fiber was blended with beaten wood pulp in a proportion of 60/40 and used for 50 g/m² web formation with an airlaid machine, and then subjected to heat treatment with an air-through dryer. The properties of the obtained airlaid nonwoven fabric are shown in Table 4.

Comparative Example 13

The same procedure was carried out as in Example 22, except that the polycondensation catalyst was changed to a 1.3% solution of antimony trioxide in ethylene glycol, the charged amount was 4.83 parts, and there was further charged 0.121 part of a 25% solution of trimethyl phosphate in ethylene glycol as a stabilizer. The results are shown in Table 4.

Comparative Example 14

The same procedure was carried out as in Example 22, except that the TB solution prepared in Example 1 alone was used as the polycondensation catalyst, and the charged amount was 1.03 parts. The polycondensation reaction time was 95 minutes. The results are shown in Table 4.

Comparative Example 15

The same procedure was carried out as in Example 22,

except that for the polycondensation catalyst, 1.03 parts of the TB solution and 2.30 parts of the P1 solution were each separately charged into the polycondensation reaction system during production of the polyester,
5 without reacting the TB solution and P1 solution. The results are shown in Table 4.

Comparative Example 16

The same procedure was carried out as in Example 23, except that for the polycondensation catalyst, 1.03 parts
10 of the TB solution and 2.3 parts of the P2 solution were each separately charged into the polycondensation reaction system during production of the polyester, without reacting the TB solution and P2 solution. The results are shown in Table 4.

Table 4

	Catalyst	Polymer quality			Color	Method	Nonwoven fabric properties	
		Catalyst content	Molar ratio of P atoms to Ti atoms	Limiting viscosity			L value/b value	
	Ti (ppm)/P (ppm)							
Example 22	TP1-2.0	52/64	2.0	0.64	81/2.0	wet	0.12	1.5
Example 23	TP2-2.0	48/60	2.0	0.64	81/2.2	wet	0.13	1.6
Example 24	TP3-1.5	32/28	1.5	0.64	81/3.0	wet	0.11	1.5
Example 25	TP4-3.0	152/260	3.0	0.64	81/2.4	wet	0.14	1.7
Example 26	TP1-2.0	52/64	2.0	0.64	81/2.0	dry	1.21	89.1
Example 27	TP1-2.0	52/64	2.0	0.64	81/2.0	airlaid	0.43	22.1
Comp.Ex.13	Sb ₂ O ₃	250 (Sb)	-	0.64	75/2.5	wet	0.11	2.4
Comp.Ex.14	T _B solution	52/-	-	0.64	81/8.0	wet	0.12	2.1
Comp.Ex.15	T _B +P ₁ solution	52/56	-	0.64	81/7.6	wet	0.14	2.5
Comp.Ex.16	T _B +P ₂ solution	52/56	-	0.64	81/7.9	wet	0.13	1.9

Example 28

The same polyethylene terephthalate chips as in Example 22 were dried and used for spinning, stretching, cutting, etc. according to ordinary methods to obtain 5 polyester drawn yarn (size: 6.6 dtex, fiber length: 51 mm, coiled three-dimensional crimps: 9.0/25 mm). The polyester drawn yarn was opened with an ordinary roller carding machine and formed into a futon card web. The waste cotton generated is shown in Table 5.

10 Example 29

The same procedure was carried out as in Example 28, except that monobutyl phosphate was used instead of monolauryl phosphate. The addition amount and conditions were also changed in the following manner.

15 After heating and dissolving 28.3 g of monobutyl phosphate in 537 g of ethylene glycol (hereinafter abbreviated as "P2 solution"), 435 g of TB solution was placed therein and a reaction product was obtained. The mixing ratio of the TB solution and P2 solution was 2.0 20 as the molar ratio of phosphorus atoms with respect to titanium atoms. This solution will hereinafter be abbreviated as "TP2-2.0 catalyst". The heating temperature was 70°C and the reaction time was 1 hour.

25 In order to analyze the obtained reaction precipitate, a portion of the reaction solution was filtered with a 5 μ pore filter to obtain the precipitated reaction product as a solid, and it was then washed with water and dried. The elemental concentration of the obtained precipitated reaction product was 30 analyzed in the same manner as above, yielding results of 17.0% titanium, 21.2% phosphorus and a phosphorus atom molar ratio of 1.9 with respect to titanium atoms. The catalyst was used for production of polyester fiber in the same manner as Example 7, after which the fibers were 35 opened with an ordinary roller carding machine and formed into a futon card web. The results are shown in Table 5.

Example 30

The same procedure was carried out as in Example 28, except that the amount of TP1 solution prepared and the amount of TB solution added were changed. The amounts prepared and added were as follows.

After heating and dissolving 31.3 g of monolauryl phosphate in 594 g of ethylene glycol (hereinafter abbreviated as "P3 solution"), 375 g of TB solution was placed therein and a reaction product was obtained. The mixing ratio of the TB solution and P3 solution was 1.5 as the molar ratio of phosphorus atoms with respect to titanium atoms. This solution will hereinafter be abbreviated as "TP3-1.5 catalyst". The catalyst was used for production of polyester fiber in the same manner as Example 1, after which the fibers were opened with an ordinary roller carding machine and formed into a futon card web. The results are shown in Table 5.

Example 31

The same procedure was carried out as in Example 29, except that the amount of TP2 solution prepared and the amount of TB solution added were changed. The amounts prepared and added were as follows.

After heating and dissolving 33.0 g of monobutyl phosphate in 627 g of ethylene glycol (hereinafter abbreviated as "P4 solution"), 340 g of TB solution was placed therein and a reaction product was obtained. The mixing ratio of the TB solution and P4 solution was 3.0 as the molar ratio of phosphorus atoms with respect to titanium atoms. This solution will hereinafter be abbreviated as "TP4-3.0 catalyst". The catalyst was used for production of polyester fiber in the same manner as Example 1, after which the fibers were opened with an ordinary roller carding machine and formed into a futon card web. The results are shown in Table 5.

Comparative Example 17

The same procedure was carried out as in Example 28, except that the polycondensation catalyst was changed to

a 1.3% solution of antimony trioxide in ethylene glycol, the charged amount was 4.83 parts, and there was further charged 0.121 part of a 25% solution of trimethyl phosphate in ethylene glycol as a stabilizer. The results are shown in Table 5.

5

Comparative Example 18

The same procedure was carried out as in Example 28, except that the TB solution prepared in Example 7 alone was used as the polycondensation catalyst, and the 10 charged amount was 1.03 parts. The polycondensation reaction time was 95 minutes. The results are shown in Table 5.

10

Comparative Example 19

15

The same procedure was carried out as in Example 28, except that for the polycondensation catalyst, 1.03 parts of the TB solution and 2.30 parts of the P1 solution were each separately charged into the polycondensation reaction system during production of the polyester, without reacting the TB solution and P1 solution. The 20 results are shown in Table 5.

20

Comparative Example 20

25

The same procedure was carried out as in Example 29, except that for the polycondensation catalyst, 1.03 parts of the TB solution and 2.3 parts of the P2 solution were each separately charged into the polycondensation reaction system during production of the polyester, without reacting the TB solution and P2 solution. The results are shown in Table 5.

Table 5

	Catalyst	Polymer quality			Wadding processing properties	
		Catalyst content	Molar ratio of P atoms to Ti atoms	Limiting viscosity	Color	Mean waste cotton
		Ti (ppm) / P (ppm)			L value/b value	(g/H)
Example 28	TP1-2.0	52/64	2.0	0.64	81/2.0	11
Example 29	TP2-2.0	48/60	2.0	0.64	81/2.2	6
Example 30	TP3-1.5	32/28	1.5	0.64	81/3.0	9
Example 31	TP4-3.0	152/260	3.0	0.64	81/2.4	10
Comp.Ex.17	Sb ₂ O ₃	250(Sb)	-	0.64	75/2.5	28
Comp.Ex.18	TB solution	52/-	-	0.64	81/8.0	0.3
Comp.Ex.19	TB+P1 solution	52/56	-	0.64	81/7.6	0.2
Comp.Ex.20	TB+P2 solution	52/56	-	0.64	81/7.9	0.13
					19	0.13

Example 32

The same polyethylene terephthalate chips as in Example 22 were dried and used to obtain polyester staple fibers with a single fiber size of 12 dtex, 8 crimps/25 mm and a crimping ratio of 30% by an ordinary method. 5 The same chips were also used as the core component, while the same catalyst was used for polymerization of a mixed acid component comprising terephthalic acid and isophthalic acid at 80/20 (mole percent) and butylene 10 glycol, and the obtained polybutylene-based terephthalate was further subjected to heated reaction at 38 wt% with 62 wt% of polybutylene glycol (molecular weight: 2000), to obtain a block copolymer polyether-ester elastomer (thermoplastic elastomer) with a limiting viscosity of 15 1.0 and a melting point of 155°C, which was used as the sheath component. Spinning, stretching, cutting, etc. were carried out for a fiber cross-sectional area core/sheath ratio of 60/40, to obtain a core-sheath conjugated polyester fiber (core/sheath ratio: 60/40, 20 fiber size: 6 dtex, 11 crimps/25 mm, crimping ratio: 8%).

The polyester staple fiber and thermal bonding conjugated polyester staple fiber were mixed in a weight proportion of 70:30 and passed twice through a roller carding machine to obtain a blended web. The web was 25 placed in a molding frame at a fixed density and subjected to heat treatment at 180°C x 15 min using a circulating hot air dryer to obtain a fiber structure with a density of 0.04 g/cm³ and a thickness of 5 cm. The properties of the obtained fiber structure were evaluated 30 and the results are shown in Table 6.

Example 33

The same procedure was carried out as in Example 32, except that monobutyl phosphate was used instead of monolauryl phosphate. The addition amount and conditions 35 were also changed in the following manner.

After heating and dissolving 28.3 g of monobutyl phosphate in 537 g of ethylene glycol (hereinafter

abbreviated as "P2 solution"), 435 g of TB solution was placed therein and a reaction product was obtained. The mixing ratio of the TB solution and P2 solution was 2.0 as the molar ratio of phosphorus atoms with respect to 5 titanium atoms. This solution will hereinafter be abbreviated as "TP2-2.0 catalyst". The heating temperature was 70°C and the reaction time was 1 hour.

In order to analyze the obtained reaction precipitate, a portion of the reaction solution was 10 filtered with a 5 μ pore filter to obtain the precipitated reaction product as a solid, and it was then washed with water and dried. The elemental concentration of the obtained precipitated reaction product was analyzed in the same manner as above, yielding results of 15 17.0% titanium, 21.2% phosphorus and a phosphorus atom molar ratio of 1.9 with respect to titanium atoms. The catalyst was used for production of polyester fiber in the same manner as Example 11, after which web formation, heat treatment, etc. were carried out to obtain a fiber 20 structure. The results are shown in Table 6.

Example 34

The same procedure was carried out as in Example 32, except that the amount of TP1 solution prepared and the amount of TB solution added were changed. The amounts 25 prepared and added were as follows.

After heating and dissolving 31.3 g of monolauryl phosphate in 594 g of ethylene glycol (hereinafter abbreviated as "P3 solution"), 375 g of TB solution was placed therein and a reaction product was obtained. The mixing ratio of the TB solution and P3 solution was 1.5 30 as the molar ratio of phosphorus atoms with respect to titanium atoms. This solution will hereinafter be abbreviated as "TP3-1.5 catalyst". The catalyst was used for production of polyester fiber in the same manner as Example 1, after which web formation, heat treatment, 35 etc. were carried out to obtain a fiber structure. The results are shown in Table 6.

Example 35

The same procedure was carried out as in Example 33, except that the amount of TP2 solution prepared and the amount of TB solution added were changed. The amounts prepared and added were as follows.

After heating and dissolving 33.0 g of monobutyl phosphate in 627 g of ethylene glycol (hereinafter abbreviated as "P4 solution"), 340 g of TB solution was placed therein and a reaction product was obtained. The mixing ratio of the TB solution and P4 solution was 3.0 as the molar ratio of phosphorus atoms with respect to titanium atoms. This solution will hereinafter be abbreviated as "TP4-3.0 catalyst". The catalyst was used for production of polyester fiber in the same manner as Example 11, after which web formation, heat treatment etc. were carried out to obtain a fiber structure. The results are shown in Table 6.

Example 36

Spinning, stretching, cutting, etc. were carried out according to ordinary methods, using chips obtained by addition copolymerization of isophthalic acid and 1,6-hexanediol with the same catalyst used for the polyester chips obtained in Example 32, to obtain core-sheath conjugated polyester fiber (core/sheath ratio: 50/50, size: 4.4 dtex, fiber length: 51 mm). The procedure of Example 11 was otherwise followed to produce polyester staple fiber, after which web formation, heat treatment etc. were carried out to obtain a fiber structure. The heat treatment temperature, however, was 150°C. The results are shown in Table 6.

Comparative Example 21

The same procedure was carried out as in Example 32, except that the polycondensation catalyst was changed to a 1.3% solution of antimony trioxide in ethylene glycol, the charged amount was 4.83 parts, and there was further charged 0.121 part of a 25% solution of trimethyl phosphate in ethylene glycol as a stabilizer. The

results are shown in Table 6.

Comparative Example 22

The same procedure was carried out as in Example 32, except that the TB solution prepared in Example 1 alone
5 was used as the polycondensation catalyst, and the charged amount was 1.03 parts. The polycondensation reaction time was 95 minutes. The results are shown in Table 6.

Comparative Example 23

10 The same procedure was carried out as in Example 32, except that for the polycondensation catalyst, 1.03 parts of the TB solution and 2.30 parts of the P1 solution were each separately charged into the polycondensation reaction system during production of the polyester,
15 without reacting the TB solution and P1 solution. The results are shown in Table 6.

Table 6

	Catalyst	Polymer quality			Fiber structure quality			
		Catalyst content	Molar ratio of P atoms to Ti atoms	Limiting viscosity	Color	Hardness N	Residual deformation with repeated compression %	
	Ti (ppm) / P (ppm)		L value/b value				Hard masses	
Example 32	TP1-2.0	52/64	2.0	0.64	81/2.0	361	7.1	5
Example 33	TP2-2.0	48/60	2.0	0.64	81/2.2	363	8.4	5
Example 34	TP3-1.5	32/28	1.5	0.64	81/3.0	360	6.9	5
Example 35	TP4-3.0	152/260	3.0	0.64	81/2.4	374	9.3	5
Example 36	TP1-2.0	52/64	2.0	0.64	81/2.0	420	12.6	5
Comp.Ex.21	Sb ₂ O ₃	250 (Sb)	-	0.64	75/2.5	397	12.4	3
Comp.Ex.22	TB solution	52/-	-	0.64	81/8.0	393	12	2
Comp.Ex.23	TB+P1 solution	52/56	-	0.64	81/7.6	309	11.1	3

Industrial Applicability

The polyester fiber structure of the present invention has satisfactory color tone (color b* value) and excellent quality, and therefore when the polyester fiber structure is a nonwoven fabric, it has particularly high practical utility for purposes which involve contact with food products, such as food product packaging materials, food filters such as black tea bags, green tea bags and coffee filters, harshness removal sheets, oil filter sheets, kitchen wiper sheets, reverse osmosis membrane base sheets, sanitary materials and beverage filter materials. It may also be applied for such purposes as various types of filters, wallpaper, sash paper, name cards, documents, household/office wipers, printing base paper, electrical material bases, carpets, engineering sheets, soundproof/insulating materials, agricultural/horticultural sheets and the like.

When the polyester fiber structure is wadding, it is suitable as various types of wadding including general purpose padding for bedding fiber products such as bed covers, bed sheets, bed pads, pillows and cushions or for stuffed goods and the like, household paddings for sofa and chair backs, and clothing or industrial resin cotton intended for thermal insulation, sound absorption or soundproofing.

When the polyester fiber structure is a fiber structure comprising main fiber made of polyester stable fiber and thermal bonding conjugated staple fiber, it is suitable for such purposes as bedding fixtures, furniture, automobile materials (cushion materials, ceiling materials, protective materials, etc.), clothing, filter materials, construction/engineering materials (soundproofing or insulating materials), agricultural materials, sanitary materials (poultices, diapers, napkins, etc.) and the like.